

**ETHYLENE/VINYL ACETATE COPOLYMERS (E/VAC) - FOURIER  
TRANSFORM INFRARED SPECTROMETRIC METHOD FOR  
DETERMINATION OF VINYL ACETATE CONTENT**

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**INTRODUCTION**

The Harmonized Commodity Description and Coding System classifies copolymers according to provisions specified in Note 4 and Subheading Note 1 to Chapter 39. Note 4 defines copolymers as all polymers in which no single monomer contributes 95% or more by weight to the total polymer content. On the other hand, those polymers in which one monomer contributes more than 95% are considered as homopolymers. In border-line situations, it is difficult to decide whether an analyzed product is a copolymer or a homopolymer. Such cases are often encountered with E/VAC copolymers having low vinyl acetate (VAC) content, where subheadings 3901.10 and 3901.30 may apply. In this instance, the precise determination of the comonomer content becomes critical.

E/VAC is widely used in industry, the applications depending on the VAC content. Examples include clear films for the packaging industry (2-5% VAC (m/m)), high performance films (7.5-12% VAC (m/m)), hot melt adhesives (21-40% VAC (m/m)), or cable engineering materials (<30% VAC (m/m)) [1].

In this work, Fourier Transform Infrared (FTIR) spectroscopy has been applied to determine percent VAC relative to the ethylene monomer unit (E) in E/VAC having a low VAC content. This technique is both fast and reliable and its usefulness has already been proven in the previous work [2-4]. A short study has been conducted to extend previous investigations by focusing on optimizing the band selection and performing statistical analysis to calculate the experimental precision error.

Commercial products, including DuPont's "Elvax", Bayer's "Baylon" and "Levapren", Dow's "Zetafax" and Quantum Chemical's "Petrothene" of known composition were used. These samples had

a stated nominal vinyl acetate content from 1.5 to 45% by weight.

## **EXPERIMENTAL**

### **1 PRINCIPLE**

The VAC content is determined by FTIR. The method consists of pressing thin films of E/VAC, recording FTIR spectra and calculating the ratio of selected optical densities (OD) corresponding to VAC and E bands. The optical densities are determined using peak heights or peak areas.

### **2 APPARATUS**

**2.1 Compression moulding press** with heated platens, capable of achieving a pressure of 4.5 MPa and a platens temperature of 170°C.

**2.2 FTIR spectrometer**, of wave number range 3700  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

#### **NOTE:**

In this study, FTIR spectra were obtained on a Perkin-Elmer 1600 spectrometer using ten scans with a resolution of 4.0  $\text{cm}^{-1}$ . Up to six different samples were measured for each nominal composition. Peak heights and peak areas were measured from a sloped baseline drawn through adjacent valleys using a GRAMS/386 software package.

### **2.3 Film holder**

## **3 PROCEDURE**

### **3.1 Preparation of films**

Mould the films using compression moulding press (2.1), lined with aluminum foil at a temperature of approximately 170°C and pressure adjusted to obtain a film thickness between 50  $\mu\text{m}$  to 100  $\mu\text{m}$  (approximately 4.5 MPa (650 psi)).

## NOTES:

1. To avoid possible thermal decomposition of the product, pressing time should be limited to 1 min.
2. To facilitate film release, (e.g. for low molecular weight E/VAC), extra layers of Kapton or Teflon [5] liner could be applied.

**3.2 Measurement**

- 3.2.1** Scan the background.
- 3.2.2** Record the spectrum using minimum of 10 scans.
- 3.2.3** Ratio the spectrum and convert into absorbance.
- 3.2.4** Select the best resolved peak among 610, 1020 or 3460  $\text{cm}^{-1}$  of the VAC bands (the complete band assignment is listed in Table 1), establish the baseline by drawing a straight line through adjacent valleys, and measure the optical density as the peak height, or for better results use peak areas (compare results in Figures 2, 3 and 4).
- 3.2.5** Repeat procedure 3.2.4 for E peak at 720  $\text{cm}^{-1}$ .
- 3.2.6** Determine the ratio of selected optical densities corresponding to VAC and E bands.

**4 EXPRESSION OF RESULTS****4.1 VAC content  $\leq$  25% (m/m)****4.1.2 Optical density determination using peak heights**

Establish the VAC content as a percentage by mass applying the ratio of optical densities determined in 3.2.6 using one of the following formulas:

$$\text{VAC\% (m/m)} = [380 \times \text{OD}(3460/720)^h - 1.1] \pm 5.2\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [11.8 \times \text{OD}(1020/720)^h + 1.6] \pm 3.2\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [58.2 \times \text{OD}(610/720)^h + 0.7] \pm 4.9\% \text{ (m/m)}$$

Where:

380, 11.8, and 58.2 represent the slope values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method;

$\text{OD}(3460/720)^h$ ,  $\text{OD}(1020/720)^h$ , and  $\text{OD}(610/720)^h$  are the optical density ratios as determined in 4.2.6 using peak heights;

-1.1, 1.6, and 0.7 represent the intercept values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method; and

$\pm 5.2\%$ ,  $\pm 3.2\%$ , and  $\pm 4.9\%$  (m/m) represent the precision error at 95% confidence level calculated from deviations of any given reading from the best linear fit (standard deviations are listed in Table 2).

#### 4.1.3 Optical density determination using peak areas

Establish the VAC content as a percentage by mass applying the ratio of optical densities determined in 3.2.6 using one of the following formulas:

$$\text{VAC\% (m/m)} = [192 \times \text{OD}(3460/720)^a + 0.3] \pm 3.1\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [6.9 \times \text{OD}(1020/720)^a + 1.5] \pm 2.8\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [90.0 \times \text{OD}(610/720)^a + 0.6] \pm 4.3\% \text{ (m/m)}$$

Where:

192, 6.9, and 90.0 represent the slope values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method;

$\text{OD}(3460/720)^a$ ,  $\text{OD}(1020/720)^a$ , and  $\text{OD}(610/720)^a$  are the optical density ratios determined in 3.2.6 using peak areas;

0.3, 1.5, and 0.6 represent the intercept values on the corresponding calibration curves (Figure 2, 3, and 4) from the least squares method; and

$\pm 3.1\%$ ,  $\pm 2.8\%$ , and  $\pm 4.3\%$  (m/m) represent the precision error at 95% confidence level calculated from deviations of any given reading from the best linear fit (standard deviations are listed in Table 2).

#### 4.2 VAC content between 25 and 45% (m/m)

Establish VAC content as a percentage by mass using the ratio of optical densities determined in 3.2.6 (using either peak heights or peak areas) and reading VAC% (m/m) directly from the corresponding calibration curve (Figure 5, 6, or 7).

### RESULTS AND DISCUSSION

The representative, expanded reference spectra of E/VAC copolymers are shown in Figure 1 while all the relevant monomer bands are included in Table 1. The following suitability considerations have been made for the band selection:

- 3460  $\text{cm}^{-1}$  This isolated VAC band is suitable, however it may be obstructed by the presence of the interfering -OH or -NH absorptions (e.g. from antioxidant additives), particularly at low VAC levels. Therefore, the use of other VAC bands may become necessary.
- 2678  $\text{cm}^{-1}$  Although reported to have been used successfully as an E band [3 and references therein], this band appeared to be an impractical choice in our method due to its complexity (it is a shoulder on a much stronger CH absorption). In particular, it is very difficult to draw a correct baseline.
- 1743  $\text{cm}^{-1}$  This band is too intense. Generally, an OD should be less than 0.7 on the absorbance scale [6].
- 1465  $\text{cm}^{-1}$  This band is not suitable because it includes bending modes of both constituent monomer units.
- 1372  $\text{cm}^{-1}$  This band is not the best choice since it includes stretches of both  $\text{CH}_3$  groups from VAC and E (branching and terminal), and it can be further obstructed by additives.

- 1250  $\text{cm}^{-1}$  This VAC band is too intense.
- 1020  $\text{cm}^{-1}$  This is a fairly well resolved, medium intensity band of VAC.
- 720  $\text{cm}^{-1}$  The band of choice for E. This peak often appears as doublet due to crystal field splitting.
- 610  $\text{cm}^{-1}$  The band has a complex character, however baseline selection can be accomplished with ease.

The VAC% (m/m) data points obtained by this method are presented in the calibration curves as an average of three to six trials (Figures 2-7). For the low vinyl acetate range i.e., between 1.5-25% (m/m), where linearity was observed, a set of equations has been constructed. These equations describe straight lines shown in Figures 2-4. The slope and the intercept parameters in these equations have been obtained from the linear least-squares method. Figures 5-7 may serve as "manual" calibration curves for VAC determination outside the linear range.

For all the band ratios throughout this study, relatively good reproducibility parameters were obtained. Peak areas generally gave better precision in VAC determinations than peak heights which were consistently manifested in lower values of the calculated precision error. These values relate to linear approximation of the experimental results and were calculated at 95% confidence level using ordinates of the Normal Distribution Curve [7].

It was found that if VAC content is below 8% by weight, the use of the overtone band at 3460  $\text{cm}^{-1}$  becomes impractical due to increasing interference from moisture and/or other hydroxylic species.

The best value of precision error of  $\pm 2.8\%$  VAC (m/m) obtained by this method (paragraph 4.1.3) indicates that the method can be routinely applied to "screen" E/VAC samples. Statistically, it means that for the given example, 95% of all the readings are expected to be accurate to within  $\pm 2.8\%$  VAC. The remaining 5% would reside outside these limits. When VAC content was back-calculated using linear equations described under Sections 4.1.2 and 4.1.3 and compared to the "original"

nominal content, the results (see Table 3) appeared well within limits of accuracy error. However, in borderline situations (practically, if VAC content is between 3 to 7% (m/m)), a more precise method should be used. The acidimetric titration which has been reported repeatable to between 0.3-0.5% (m/m) seems to be good alternative, but its precision error remains to be determined [2].

### CONCLUSION

For the FTIR analysis of E/VAC, it was found that the most precise results were obtained by determining the optical density ratio at  $1020\text{ cm}^{-1}/720\text{ cm}^{-1}$  and by using the technique of peak integration. The method's precision was limited to  $\pm 2.8\%$  VAC.

### ACKNOWLEDGEMENT

The author would like to thank the following persons from the Canadian Customs Laboratory for their contributions in preparation of this method: Mr. André Côté for invaluable assistance in electronic data transfer, and Mr. Allan Granville for fruitful discussions on statistical analysis.

Special thanks are directed to Mr. Ronald E. Roller, Research Specialist at Quantum Chemical, USI Division in Cincinnati, Ohio for providing valuable E/VAC standards with low VAC content.

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5. DuPont's registered trade names for polyimide based on pyromellitic acid dianhydride and 4,4'-diaminodiphenyl ether, and polytetrafluoroethylene, respectively.
6. A. L. Smith, "Trace Analysis by Infrared Spectroscopy" in J. D. Christian and J. B. Callis, Trace Analysis: Spectroscopic Methods for Molecules, J.Wiley, New York, 1986, page 249.
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**Table 1****Comonomer Contributions and IR Band Assignments of  
E/VAC Copolymers**

ethylene	vinyl acetate	band interpretation
cm <sup>-1</sup>		
	3460	overtone of C=O at 1743 cm <sup>-1</sup>
2678		CH <sub>2</sub> stretching
	1743	C=O stretching
1465		CH <sub>2</sub> bending
	1372	CH <sub>3</sub> bending
	1250	C-O stretching of (C=O)-O
	1020	C-O stretching of O-CH
720		(CH <sub>2</sub> ) <sub>n</sub> n≥4 rocking
	610	CH <sub>3</sub> -(C=O)-O bending

**Table 2****Standard Deviations of the Optical Density Ratios<sup>†</sup>**

Optical Density Ratio	Standard Deviation	
	height	area
3640 cm <sup>-1</sup> /720 cm <sup>-1</sup>	0.00692	0.00815
1020 cm <sup>-1</sup> /720 cm <sup>-1</sup>	0.140	0.205
610 cm <sup>-1</sup> /720 cm <sup>-1</sup>	0.0432	0.0246

<sup>†</sup>based on deviation of any given reading from the least-squares line

**Table 3****Determination of Vinyl Acetate Content in E/VAC Copolymer**

nominal <sup>a</sup>	Vinyl Acetate Weight Percent					
	calculated <sup>b</sup>					
	3460/720		1020/720		605/720	
1.5	ND <sup>c</sup>		2.0	(2.5)	2.1	(2.2)
2.5	ND		2.6	(3.3)	3.0	(2.7)
4.5	ND		3.1	(4.0)	4.7	(4.3)
8	7.4	(6.9)	8.5	(8.0)	7.1	(7.1)
9	9.1	(9.8)	9.7	(9.1)	9.3	(9.9)
12	12.6	(12.4)	10.1	(9.6)	11.1	(11.1)
15	15.3	(14.6)	15.7	(14.7)	13.6	(13.5)
18	18.0	(18.8)	18.3	(17.8)	18.3	(18.7)
25	24.9	(25.6)	24.9	(26.6)	26.2	(25.7)

<sup>a</sup>as claimed by the manufacturer

<sup>b</sup>calculated for the indicated optical density ratios using peak areas and linear equations from paragraph 4.1 (numbers in parentheses represent results obtained using corresponding peak heights)

<sup>c</sup>result not determined

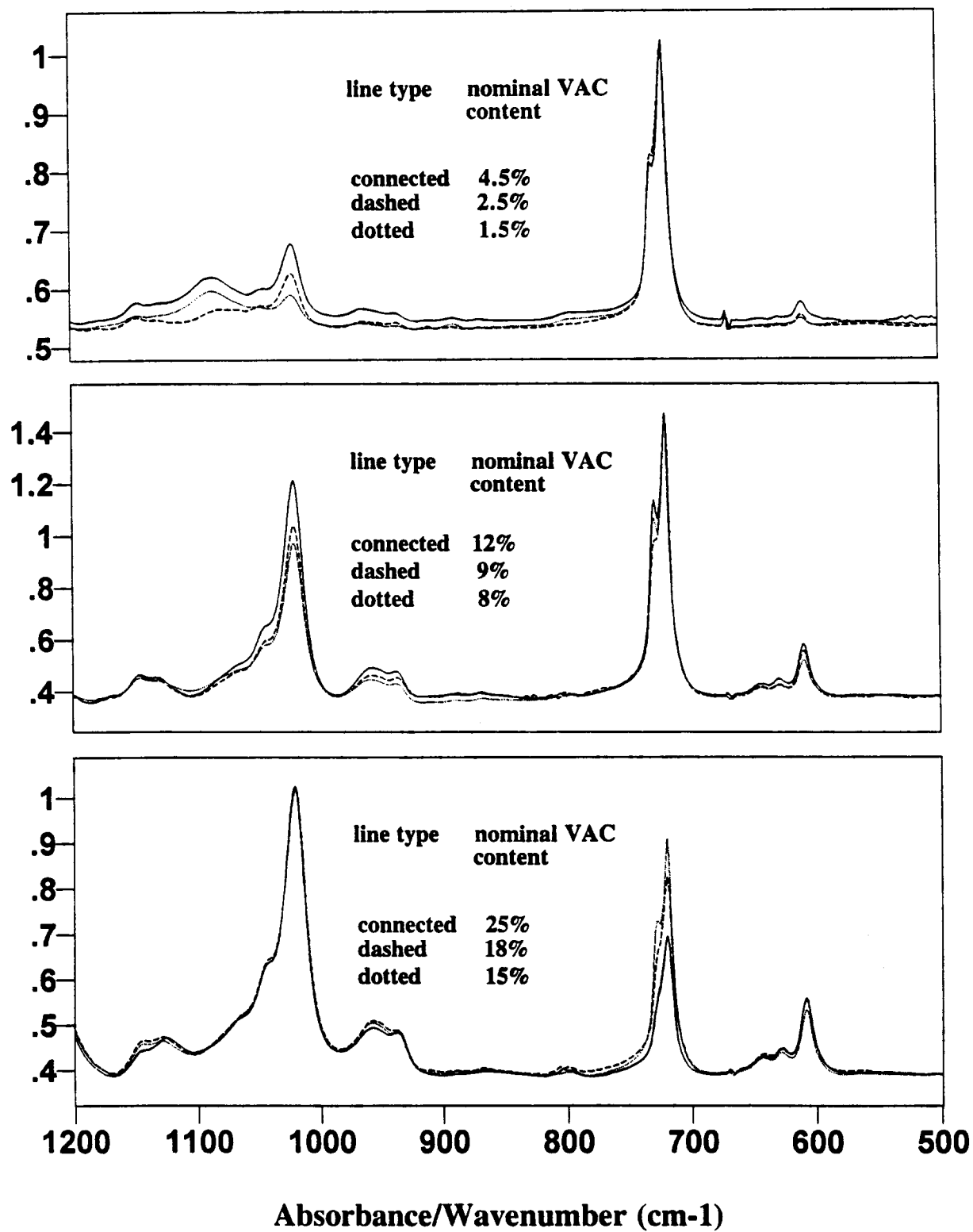
**Figure 1**

Figure 2

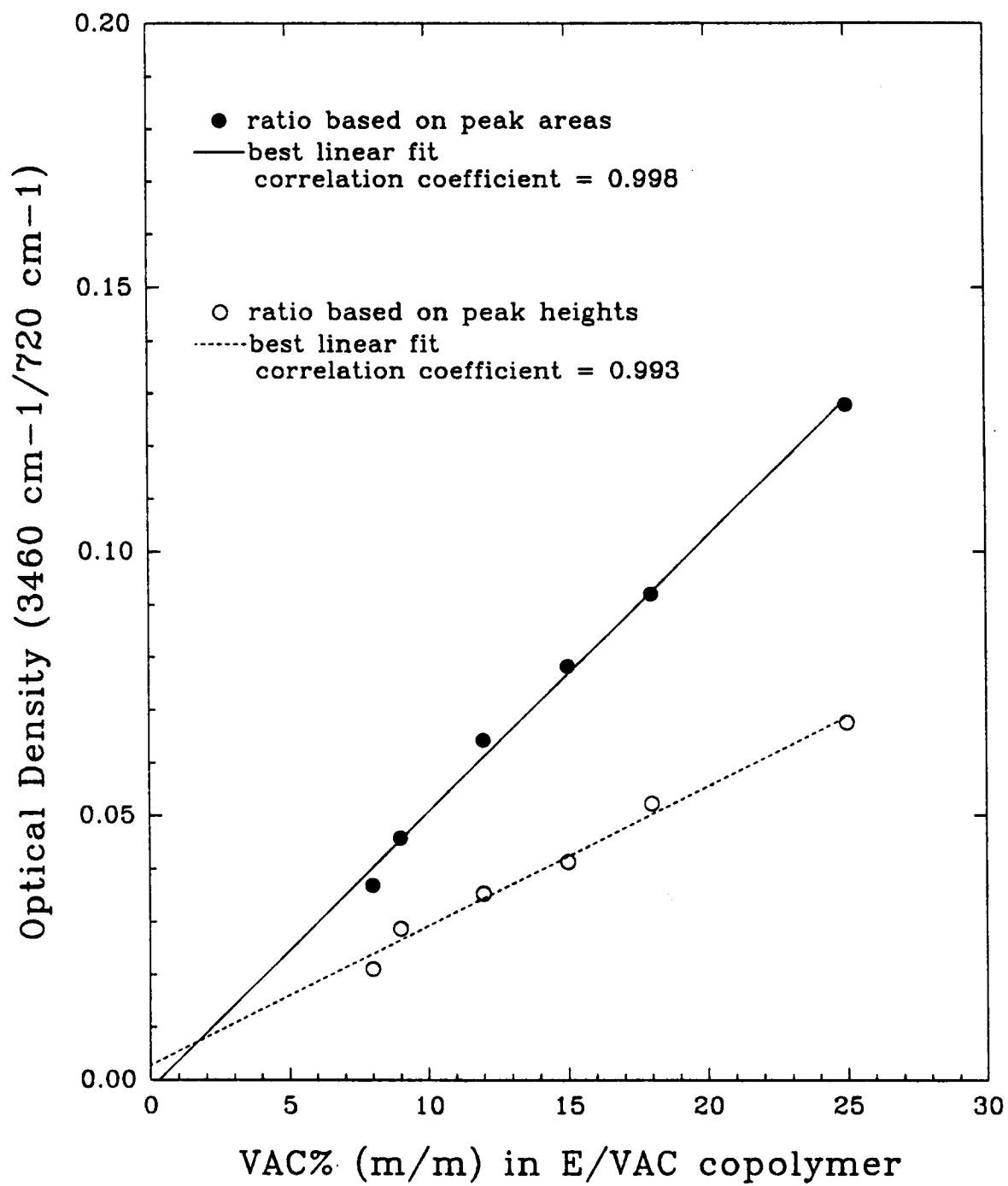


Figure 3

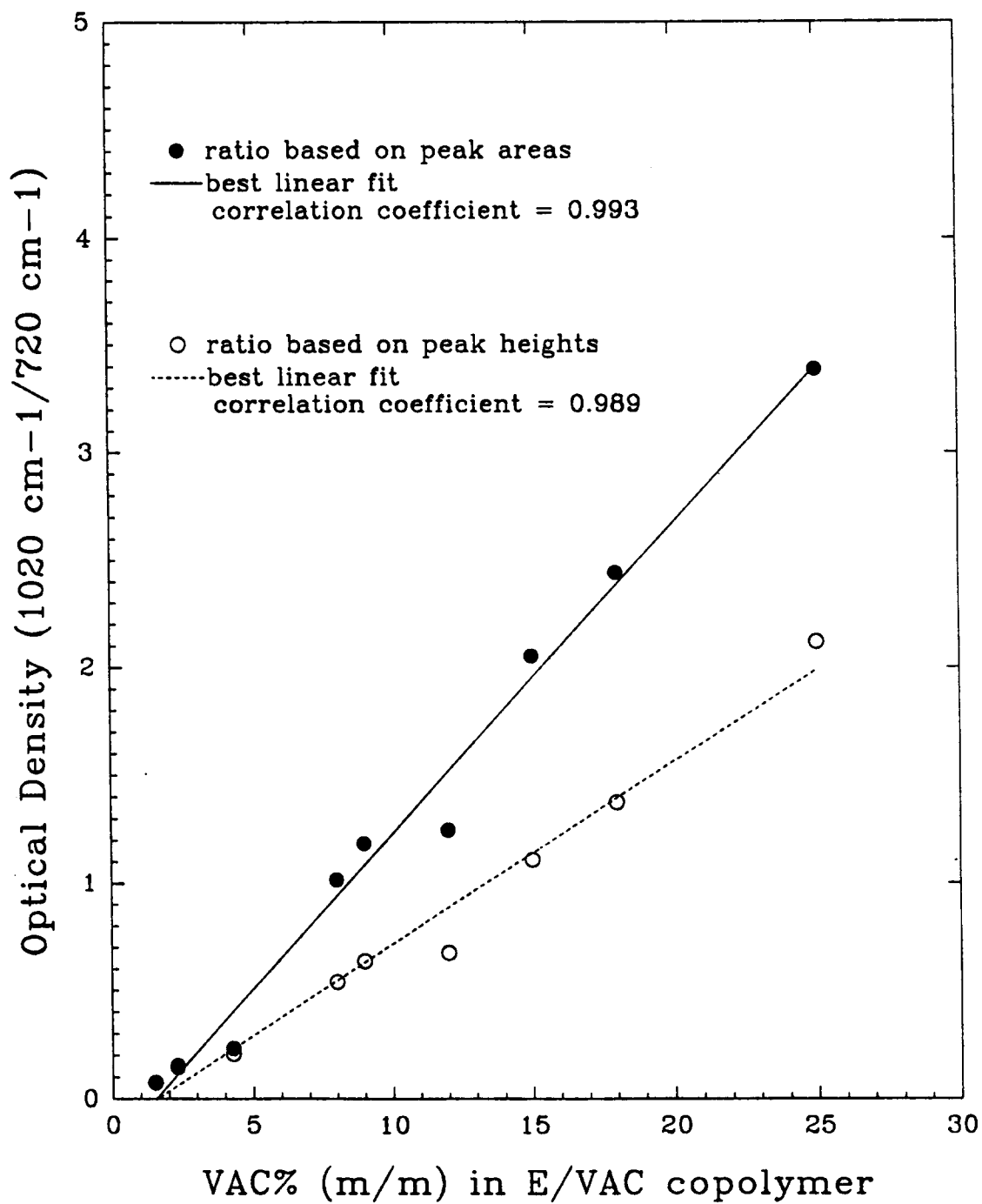


Figure 4

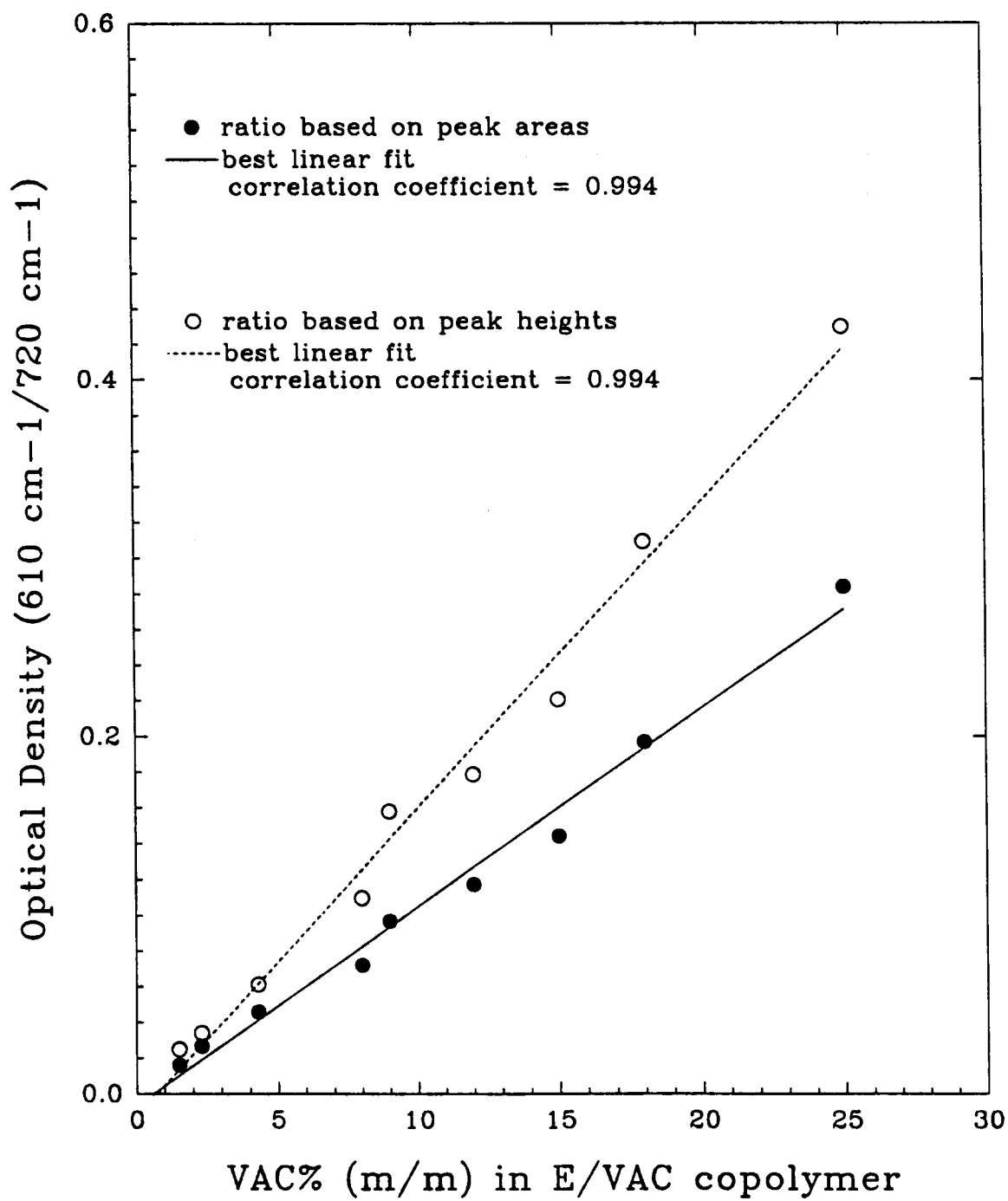
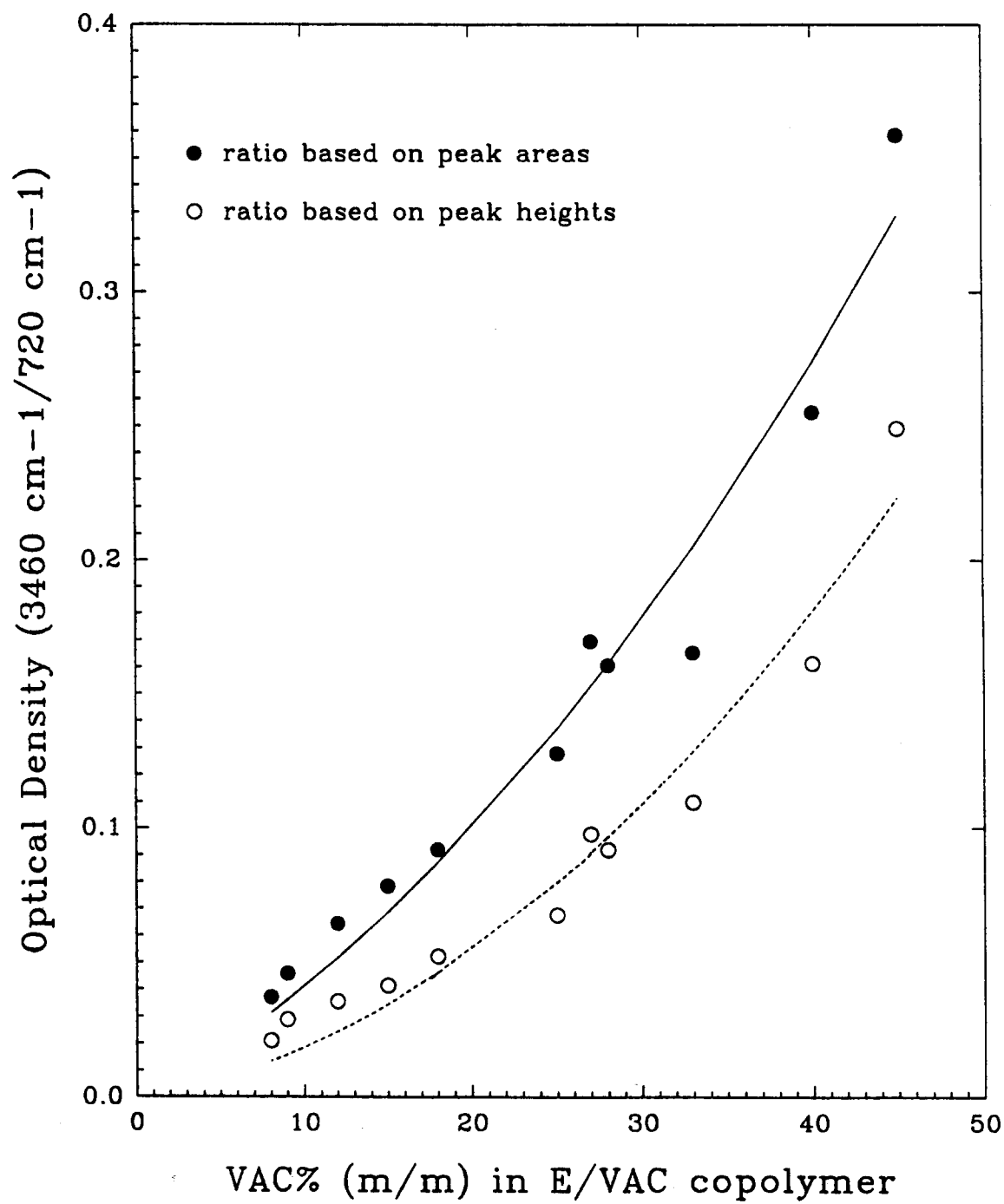


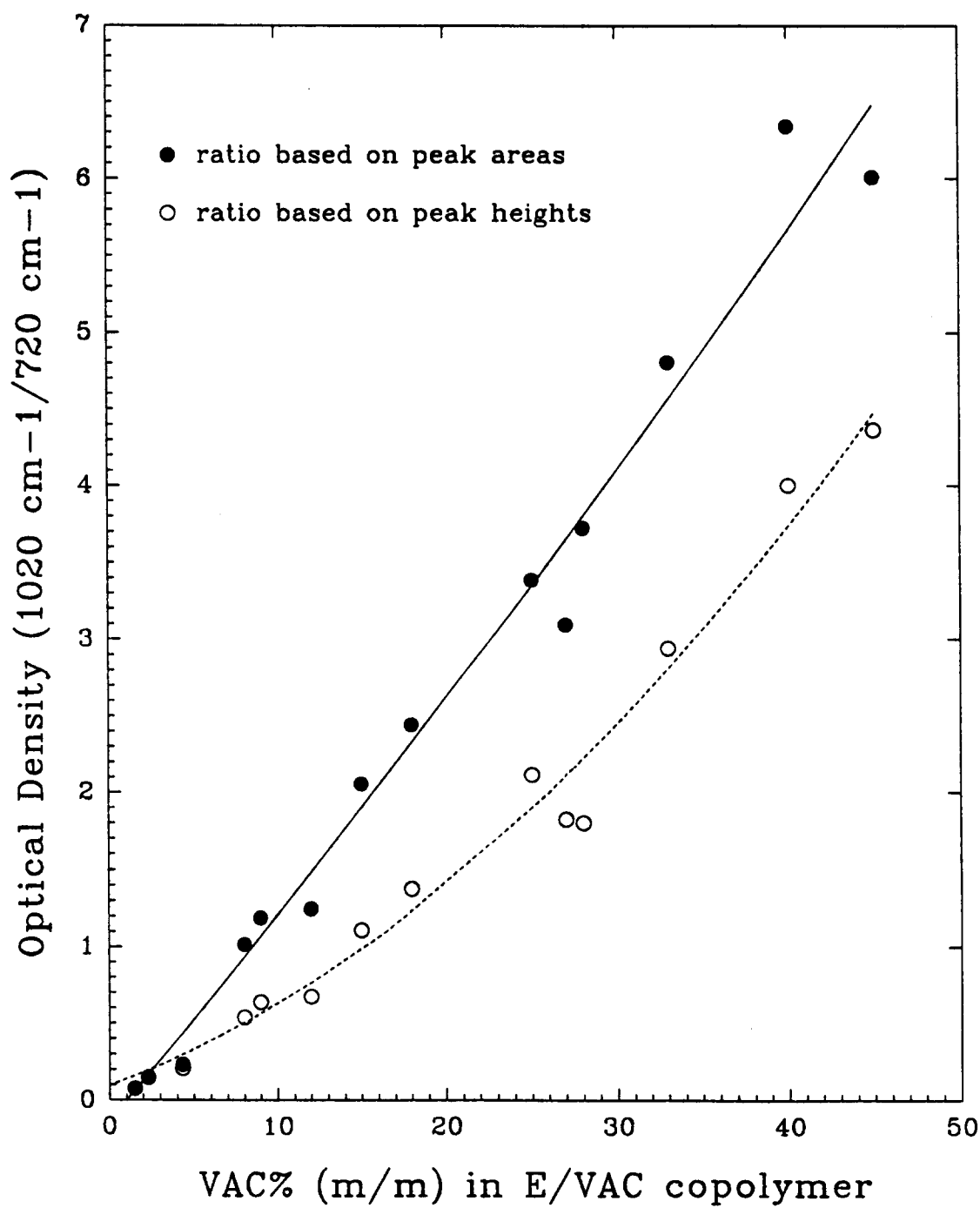
Figure 5



points connected for clarity

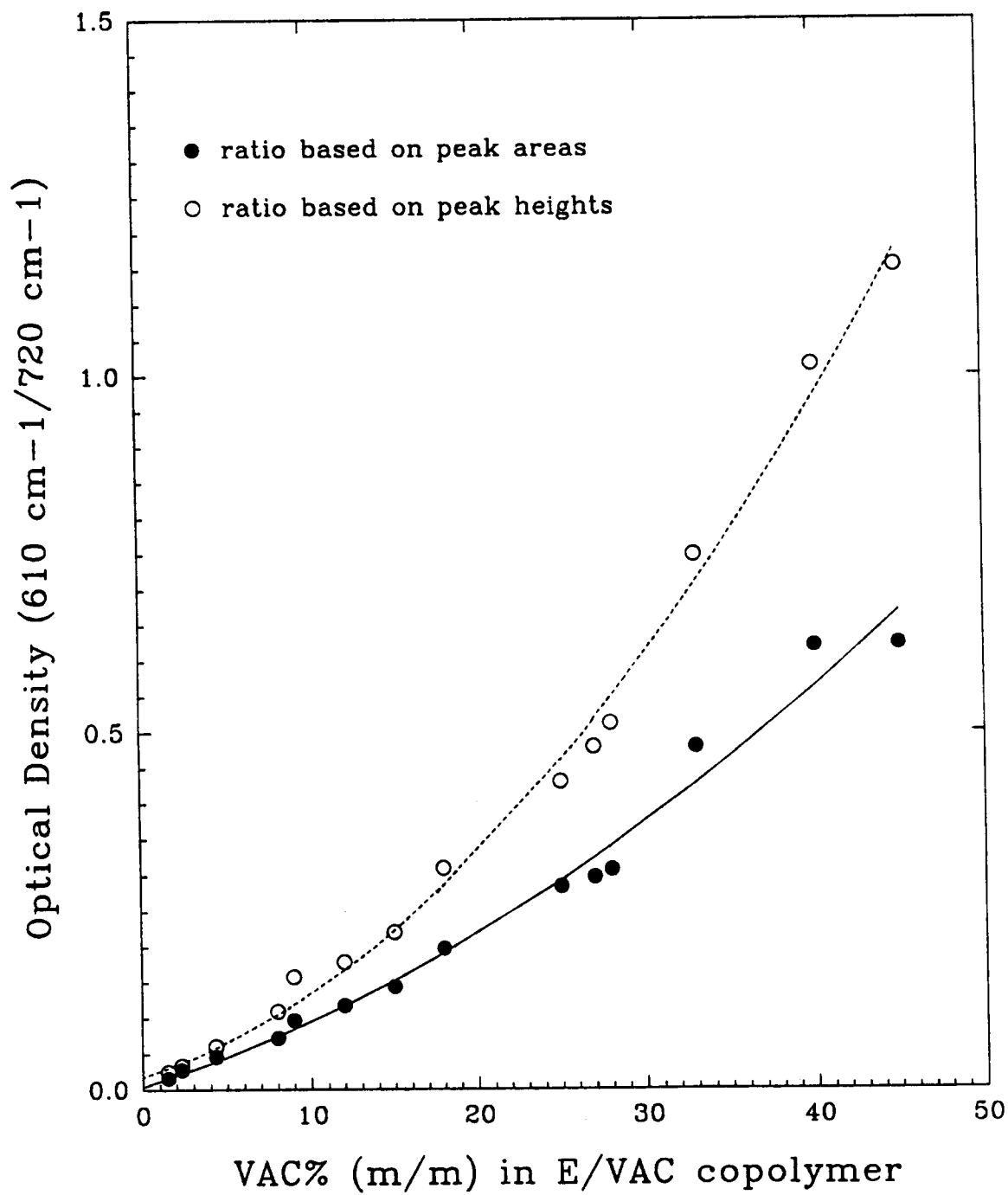


Figure 6



points connected for clarity

Figure 7



points connected for clarity